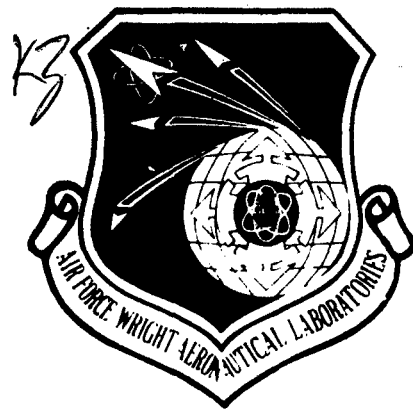


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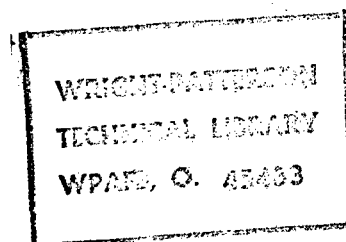
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ACETYLENE TERMINATED PHENYLENE (R)  
THERMOSET SYSTEMS

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Polymer Branch  
Nonmetallic Materials Division



June 1981

Final Report for Period January 1979 to October 1979

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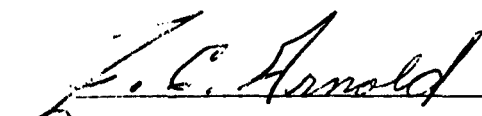
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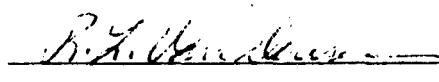
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This technical report has been reviewed and is approved for publication.

  
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFWAL-TR-81-4006	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ACETYLENE TERMINATED PHENYLENE ® THERMOSET SYSTEMS		5. TYPE OF REPORT & PERIOD COVERED Final Report January 1979-October 1979
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) G.A. Loughran, B.A. Reinhardt E.J. Soloski, F.E. Arnold		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Materials Laboratory (AFWAL/MLBP) Air Force Wright Aeronautical Laboratories Wright-Patterson Air Force Base, Ohio 45433		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62102F/2419/04 24190415
11. CONTROLLING OFFICE NAME AND ADDRESS Materials Laboratory (AFWAL/MLBP) Air Force Wright Aeronautical Laboratories Wright-Patterson Air Force Base, Ohio 45433		12. REPORT DATE June 1981
		13. NUMBER OF PAGES 30
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Acetylene Terminated Oligomers Addition Cure		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  A series of acetylene terminated phenylene ® thermoset systems have been synthesized and their thermal and thermal mechanical properties correlated with molecular structure. The synthesis provided the materials as a mixture of monomer and oligomer. The monomer was separated from the oligomer by means of column chromatography. Their glass transition temperature before and after thermal cure were determined using DSC plus thermomechanical analyses (TMA). The thermal and thermooxidative properties of the materials were		

20. evaluated with cured monomers by thermogravimetric analysis and isothermal aging in air, at 600°F.

## FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2419 "Aerospace Structural Materials," Task No. 241904 Work Unit Directive 24190415, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. F. E. Arnold as the AFWAL Project Scientist. Co-authors were Mr. G. A. Loughran, Mr. B. A. Reinhardt and Dr. F. E. Arnold, Materials Laboratory, (AFWAL/MLBP) and Mr. E. J. Soloski, University of Dayton Research Institute.

This report covers research conducted from January 1979 to October 1979.

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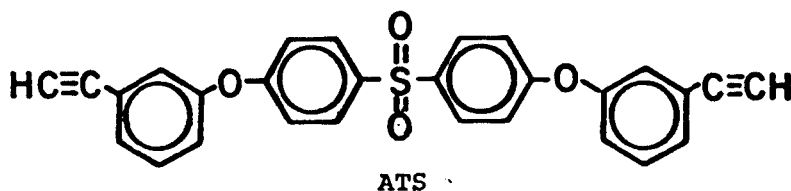


## SECTION I

### INTRODUCTION

A substantial effort in this laboratory has been directed toward the synthesis and characterization of acetylene terminated oligomers for use as addition curable moisture resistant thermoset systems. Early work on the acetylene terminated phenylquinoxalines (References 1,2) demonstrated the moisture insensitivity of the product generated from the thermal cure. Kinetic studies (Reference 3) suggest a thermally induced free-radical chain mechanism leading to a conjugated polyene. It is felt that subsequent higher temperature reactions occur with the conversion of the conjugated polyene to various aromatized products.

More recent studies (Reference 4) have been concerned with the utilization of acetylene functionality and designing a system which would have all the processing criteria of an epoxide system. The study provided the first phenylene  $\textcircled{R}$  system which incorporates a phenyl-sulfone backbone and has been referred to as ATS. Sponsored research (Reference 5) in our laboratory for lower cost precursors to ATS has led to the synthesis of bromo-endcapped phenylsulfone oligomers via the Ullmann ether synthesis. The bromo-oligomers can be converted to the acetylene terminated system by the conventional ATS synthesis.



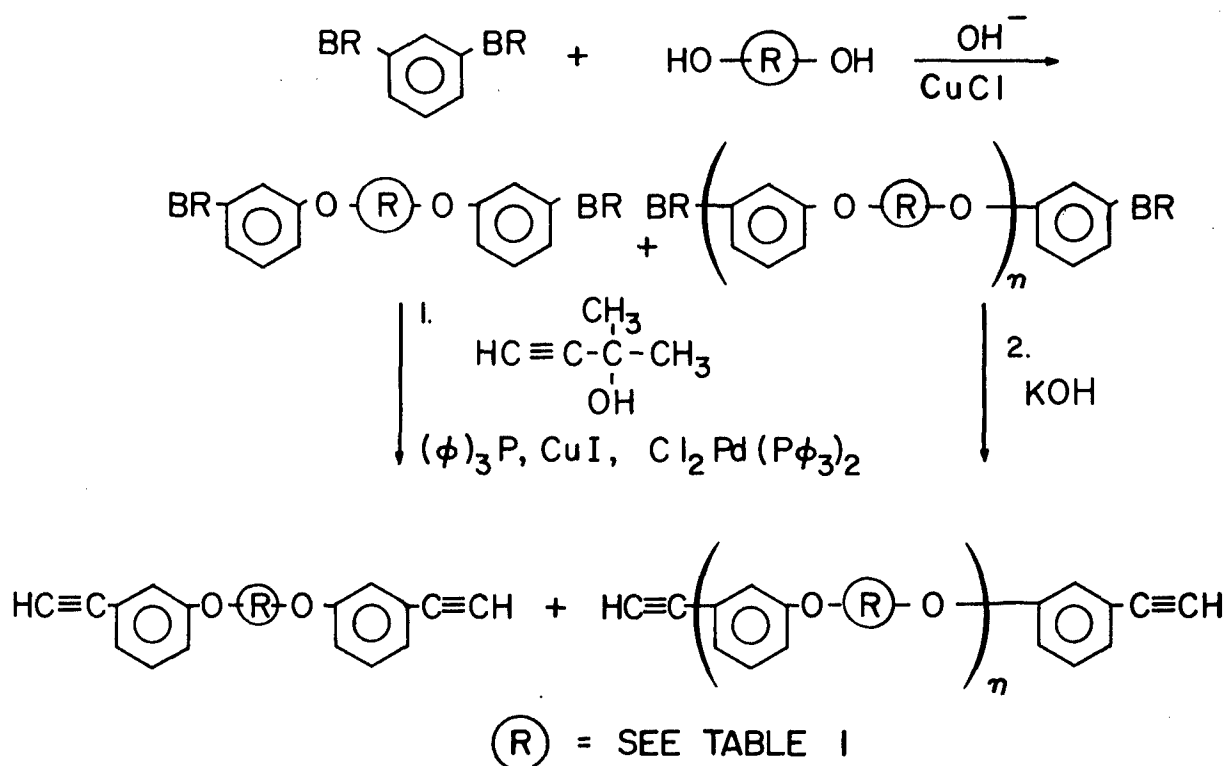
The objective of this work is to synthesize a series of AT-phenylene  $\textcircled{R}$  systems for the purpose of correlating their thermal and thermal mechanical properties versus molecular structure.

## SECTION II

### RESULTS AND DISCUSSION

## 1. SYNTHESIS

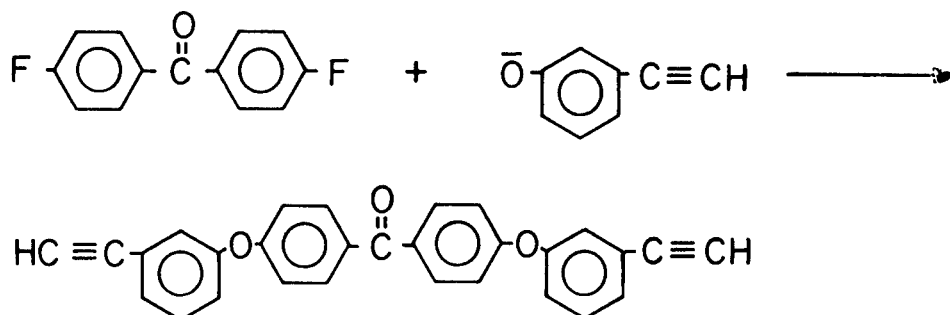
The synthesis of the oligomers was carried out by the reaction of various aromatic bis-diols with m-dibromobenzene leading to a series of bromo-endcapped phenylene (R) systems. Pyridine was used as the solvent for the reactions, and anhydrous potassium carbonate was utilized to generate the metallic salts of the bis-diols. In an effort to promote low molecular weight oligomers, the molar ratio of m-dibromobenzene to aromatic bis-diol used in the synthesis was 4 to 1. In general, the amount of monomer obtained from the 4/1 ratio was from 30-50 weight percent (Table 1) with the dimer being the second most prevalent oligomer.



The bromo-endcapped oligomers were converted to the acetylene terminated systems by the reaction with 2-methyl-3-butyn-2-ol, utilizing the catalyst system composed of triphenylphosphine,

bis-triphenylphosphine palladium chloride, and cuprous chloride. Conversion of the generated butyn-adducts to the acetylene functionality was carried out by hydrolytic displacement of acetone with potassium hydroxide in toluene.

The benzophenone system was also prepared by the reaction of m-hydroxyphenylacetylene with 4,4'-difluorobenzophenone. The synthesis allowed an independent method of obtaining pure monomer which could be compared with the monomer obtained from the Ullmann ether synthesis.



## 2. THERMAL MECHANICAL PROPERTIES

The synthesis provided the AT-phenylene (R) systems as a mixture of monomer and oligomer. The monomer was separated from the oligomer by means of column chromatography. Samples of monomer and monomer/oligomer were cured four hours at 350°F followed by one hour at 425°F, under a nitrogen atmosphere. Their glass transition temperatures before and after cure were determined using DSC plus thermomechanical analysis (TMA). The results of the thermo-analytical measurements are summarized in Table 1.

As can be seen, the Tg's of the pure monomers are all at 0°C or below with the exception of the benzophenone and biphenyl systems which have crystalline melting points. The crystallinity of the benzophenone system could be removed by heating the material beyond its melting point (~90°C) and cooling. The resulting material was amorphous with a Tg of 3°C. The biphenyl system with a Tm of 109°C does not lose its crystallinity when heated beyond its melting point. Cooling and heating

showed a polymorphous crystalline form with a  $T_m$  of  $90^\circ\text{C}$ , which appeared more stable, persisting through several heating and cooling cycles. The DSC studies of the uncured monomer/oligomer samples showed the presence of the oligomer generally to be beneficial with only small changes noted in the  $T_g$ 's. The greatest change was noted with the biphenyl system which was no longer crystalline having a  $T_g$  of  $-14^\circ\text{C}$ .

The materials after cure showed  $T_g$ 's at or above the cure temperature except for the biphenyl and perfluoroisopropyl systems with  $T_g$ 's well below cure temperature. DSC studies on all the cured samples indicate incomplete cure with substantial exotherms still evident. Samples of the benzophenone and biphenyl monomeric moieties were cured at  $500^\circ\text{F}$  for 16 hours and their DSC's showed no evidence of exotherm in the  $250^\circ\text{C}$  region. An exotherm at  $350^\circ\text{C}$  (Figure 1) was indicated for the samples which was related to the thermal decomposition of the materials. Thermogravimetric-mass spectral analysis was performed in vacuum on the benzophenone system at the same heating rate as the DSC scan. The ion intensity as a function of temperature is shown in Figure 2 and indicates that thermal decomposition starts at approximately  $350^\circ\text{C}$  with the evaluation of phenol, biphenol, and water.

### 3. THERMAL PROPERTIES

The thermal and thermooxidative properties of the materials were evaluated with cured monomers by thermogravimetric analysis (Figures 3 and 4) and isothermal aging in air, at  $600^\circ\text{F}$  (Figure 5). As can be seen, the most stable systems of those evaluated were the biphenyl and diphenylperfluoroisopropyl. All the materials, except for the diphenylsulfide system, undergo initial air oxidation as indicated by early weight gain in the isothermal aging studies. This is most likely due to the air oxidation of residual acetylene groups, since the materials were not fully cured at  $425^\circ\text{F}$ . Isothermal aging of the samples which were cured at  $500^\circ\text{F}$  for 16 hours did not show an early gain in weight (Figure 6).

## SECTION III

## EXPERIMENTAL

Analytical infrared spectra were obtained on all monomers using Perkin-Elmer 621. The infrared spectra are shown in Figures 7-12.

## 1. 1,3-BIS(3-BROMOPHENOXY) BENZENE

A mixture of 47.0g (0.20 mole) of m-dibromobenzene 10.0g (0.091 mole) of resorcinol, 34.5g (0.25 mole) of anhydrous potassium carbonate, and 0.6g of cuprous iodide in 100 ml of pyridine was heated at reflux under nitrogen for 24 hours. The reaction mixture was cooled and poured into 1000 ml of 10% HCl. Methylene chloride (200 ml) was then added and the organic layer separated. The organic layer was washed with two 100 ml portions of water, dried over anhydrous magnesium sulfate, and reduced in volume under reduced pressure to produce a dark viscous oil. The oil was dissolved in n-hexane and chromatographed on a 5cm x 50cm dry silica gel column (quartz) using hexane as the eluent. The second fluorescent band was collected and the solvent removed at 60° under reduced pressure to give 10.4 (27.2%) of a colorless viscous oil.

Analysis Calc'd for  $C_{18}H_{12}O_2Br_2$ : C, 51.46; H, 2.88; Br, 38.04

Found : C, 51.23; H, 2.50; Br, 37.73

## 2. 1,3-BIS(3-ETHYNYLPHENOXY) BENZENE

A mixture of 12.60g (0.03 mole) of 1,3-bis-(m-bromophenoxy)-benzene, 6.03g (0.072 mole) of 2-methyl-3-butyne-2-ol, and 100 ml of triethylamine was degassed by passing nitrogen through the solution for 20 minutes. To the reaction mixture was then added 0.03g (0.042 mmol) of bis-triphenylphosphine palladium II dichloride, 0.13g (0.624 mmol) of cuprous iodide, and 0.30g (1.14 mmol) of triphenylphosphine. The temperature of the reaction mixture was raised to 80°C and maintained there for 24 hours. The reaction was then cooled to room temperature and the triethylamine removed under reduced pressure. The resulting yellow-red oil was chromatographed on a 5cm x 60cm dry silica gel column (quartz) using 1:1 hexane-ether as the eluent. The second fluorescent band was collected (appears yellow on the column). The solvent was removed under reduced

pressure to yield 10.6g (83%) of a dark viscous oil. The product was used in the next step of the reaction sequence without further purification.

A mixture of 10.6g of the bis-butynol adduct and 0.75g of KOH in 20 ml of anhydrous methanol were added to 100 ml of toluene and heated to reflux under nitrogen. The methanol and 40 ml of the toluene were then removed by distillation over a period of two hours. The reaction was monitored by TLC on silica gel plates containing fluorescent indicator using 3:1 hexane-methylene chloride as the developing solvent. The product appeared as the first spot to be eluted. The reaction was judged to be complete when no starting material appeared at the origin of the TLC plate after development. After a total reaction time of two hours, the reaction mixture was cooled, and the toluene removed at 35°C under reduced pressure. The red viscous residue was chromatographed on a dry 5cm x 60cm column (quartz) of silica gel using 3:1 hexane-methylene chloride. The first large fluorescent band was collected and the solvent removed at 50°C under high vacuum. The last traces of hexane were removed by pumping on the yellow oil for 18 hours at 0.2 mm pressure. The yield of pure product was 6.1g (79%).

Analysis Calc'd for  $C_{22}H_{14}O_2$ : C,85.07; H,4.54  
Found: C,84.72; H,4.23

### 3. 4,4'-BIS(3-ETHYNYLPHENOXY) BENZOPHENONE

A solution containing 250 ml of dry DMSO 5.3g (0.04 mole) of 3-hydroxyphenylacetylene, 3.27g (0.15 mole) of 4,4'-difluorobenzophenone, and 12.53g of anhydrous potassium carbonate was stirred under a nitrogen atmosphere for 24 hours at 80°C. The reaction mixture was cooled and poured into 250 ml of distilled water and extracted with benzene. The benzene extract was filtered through a bed of silica gel and the benzene was removed under reduced pressure to give 6g (99%Y) of a white crystalline solid. The product on crystallization from cyclohexane exhibited a m.p. of 84-85°C.

Analysis Calc'd for  $C_{29}H_{18}O_3$ : C,84.04; H,4.38  
Found: C,83.65; H,4.09

## 4. 4,4'-BIS(3-BROMOPHENOXY) BIPHENYL

A mixture of 58.9g (0.25 mole) of m-dibromobenzene 16.7g (0.09 mole) of 4,4'-dihydroxybiphenyl, 69.1g (0.05 mole) of anhydrous potassium carbonate, and 0.80g of cuprous iodide in 100 ml of pyridine was heated at reflux under nitrogen for 24 hours. The reaction mixture was cooled and poured into 1000 ml of 10% HCl. Methylene chloride (200 ml) was then added and the organic layer separated. The organic layer was washed with 2 - 100 ml portions of water, dried over anhydrous magnesium sulfate, and reduced in volume under reduced pressure to produce a dark viscous oil. The oil was dissolved in  $\text{CHCl}_3$ , and placed on silica gel. The impregnated silica gel was placed at the top of a 5cm x 50cm dry silica gel column and the column eluted with 4:1 hexane-chloroform to remove unreacted m-dibromobenzene. The solvent was then changed to 2:1 hexane-chloroform and the monomeric dibromocompound removed. The solvent was changed to pure chloroform to elute the oligomeric dibromocompound. The yield of monomeric dibromocompound was 8.79g (mp. 89-92°). The yield of oligomeric dibromocompound was 13.76g (viscous oil), weight ratio of monomeric/oligomeric 1/1.56.

Analysis Calc'd for  $\text{C}_{24}\text{H}_{16}\text{O}_2\text{Br}_2$ : C, 58.09 H, 3.25  
Found: C, 58.32 H, 3.16

## 5. 4,4'-BIS(3-ETHYNYLPHENOXY) BIPHENYL

A mixture of 8.76g (17.7 mmol) of monomeric dibromocompound, 13.86g oligomeric dibromocompound, 7.15g (84.61 mmol) of 2-methyl-3-butyn-2-ol, 0.03g (0.042 mmol) of bis-triphenyl-phosphine palladium II dichloride, 0.12g (0.62 mmol) of cuprous iodide, 0.30g (1.14 mmol) of triphenyl phosphine, and 130 ml of triethylamine were degassed for 20 minutes with nitrogen. The above mixture was heated to reflux for 24 hours. The reaction mixture was cooled and the triethylamine removed under reduced pressure. The resulting oil was placed on silica gel using methylene chloride. The impregnated silica gel was dried and placed at the top of a dry silica gel column and eluted with 3:1 ether-hexane to remove any dibromo starting material and then with ethyl acetate to remove all bis-butynol adduct products. Yield: 24.6g of a dark viscous oil which was used in the next step of the reaction sequence without further purification.

A mixture of 24.6g of the bis-butynol adduct and 1.40g of KOH in 20 ml of anhydrous methanol were added to 200 ml of toluene and heated to reflux under nitrogen. The methanol and 120 ml of the toluene were then removed by distillation over a period of two hours. The reaction was monitored by TLC on silica gel plates containing fluorescent indicator using chloroform as the developing solvent. The product appeared as the first spot to be eluted. The reaction was judged to be complete when no starting material appeared at the origin of the TLC plate after development. After a total reaction time of two hours, the reaction mixture was cooled, and the toluene removed at 35°C under reduced pressure. The red viscous residue was chromatographed on a dry 5cm x 60cm column (quartz) of silica gel using chloroform. The first large fluorescent band was collected and the solvent removed at 50°C under high vacuum. The yield of pure product was 11.8g.

Analysis Calc'd for  $C_{28}H_{18}O_2$ : C,87.02; H,4.69

Found: C,86.90; H,4.24

#### 6. 4,4'-BIS(3-BROMOPHENOXY) DIPHENYLSULFIDE

To one liter of dry pyridine was added 33.4g (0.15 mole) of thiodiphenol, 110.5g (0.47 mole) of m-dibromobenzene, 21.6g of cuprous iodide, and 55.2g of anhydrous potassium carbonate. The mixture was heated to reflux under a nitrogen atmosphere and maintained at reflux for 144 hours. The progress of the reaction was monitored by TLC following the disappearance of thiodiphenol. The volume of pyridine was reduced to 200 ml and the reaction mixture treated with 500 ml of a 12% aqueous sulfuric acid solution. Extraction of the aqueous layer with 250 ml of hexane removed the excess m-dibromobenzene followed by an ether extraction to remove 76.9g (95%) of crude product. The amber oil was chromatographed on silica gel using an elution solvent of three parts hexane/one part methylene chloride. The first band contained 29.45g of monomer as a white crystalline compound MP 63-67°C and the second band yielded 17.73 of oligomer, primarily dimer.

Analysis Calc'd for  $C_{24}H_{16}O_2Br_2$ : C,54.57; H,3.05; S,30.25

Found: C,54.56; H,2.79; S,30.33

Analysis Calc'd for  $C_{42}H_{28}O_4S_2Br_2$ : C,61.46; H,3.45; Br,19.47

Found: C,61.77; H,3.02; Br,19.99



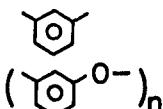
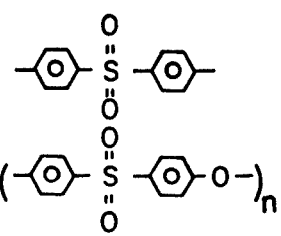
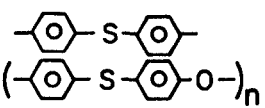
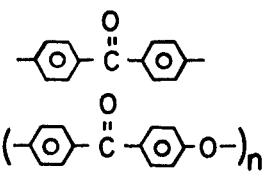
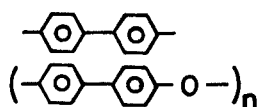
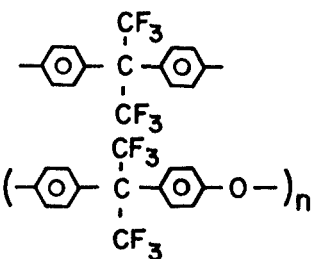
## 7. 4,4'-BIS(3-ETHYNYLPHENOXY) DIPHENYLSULFIDE

A mixture of 12.15g (0.023 mole) of 4,4'-bis(3-bromophenoxy) diphenylsulfide, 5.35g (0.064 mole) of 2-methyl-3-butyn-2-ol, and 175 ml of triethylamine was degassed by refluxing under nitrogen for one hour, then cooled to room temperature. To the reaction mixture was then added 0.05g of bis-triphenyl-phosphine, and 0.05g of cuprous iodide. The reaction mixture was refluxed for 16 hours, and allowed to cool to room temperature. The precipitated amine hydrobromide was filtered off and the filtrate passed through a bed of silica gel. The clear yellow filtrate was transferred to a flask and the solvent removed under reduced pressure leaving a viscous orange residue. This material was dissolved in 200 ml of methylene chloride and extracted with dilute (7.5%) hydrochloric acid. On removal of the methylene chloride, under reduced pressure, was obtained 9.2g (75%) of 4,4'-bis[3-(3-methyl-3'-hydroxy-1'-butynylphenoxy)]-diphenylsulfide, m.p. 48-50°C.

To a mixture of 9.02g (0.017 mole) of the bis-butynol adduct dissolved in 250 ml of toluene was added a solution containing 2g of potassium hydroxide dissolved in 20 ml of methanol. The mixture was heated to reflux under a nitrogen atmosphere, and the methanol and 200 ml of toluene was removed by distillation. On removal of the remaining toluene, under reduced pressure, was obtained 6.2g of crude product (88.%Y). This was chromatographed on silica gel using 10:1 hexane-ether mixture to give 4.1g of pure product.

Analysis Calc'd for  $C_{28}H_{18}O_2S$ : C, 80.35; H, 4.34; S, 7.66  
Found: C, 79.84; H, 4.03; S, 7.51

**TABLE I**  
**PHENYLENE (R) - AT SYSTEMS**  
**THERMAL & THERMOMECHANICAL PROPERTIES**

#	STRUCTURE (R)	RATIO mono/olig	DSC		CURED* DSC	TMA
			UNCURED T <sub>m</sub>	T <sub>g</sub>		
1		50/50	-39 -46		255 exo 210 exo	249 E 108 E
2		50/50		0 -1	210 exo 215 exo	252 E 266 E
3		65/35	-35 -32		215 exo 210 exo	232 E 155 E
4		40/60	85 -10	3	225 exo ~210 exo	263 E 53 E
5		40/60	109 -12		215 exo 230 exo	160 E 215 E
6		40/60	-15 -5		220 exo 225 exo	155 E 154 E

\* CURED: 4 HRS @ 350°F  
 1 HRS @ 425°F

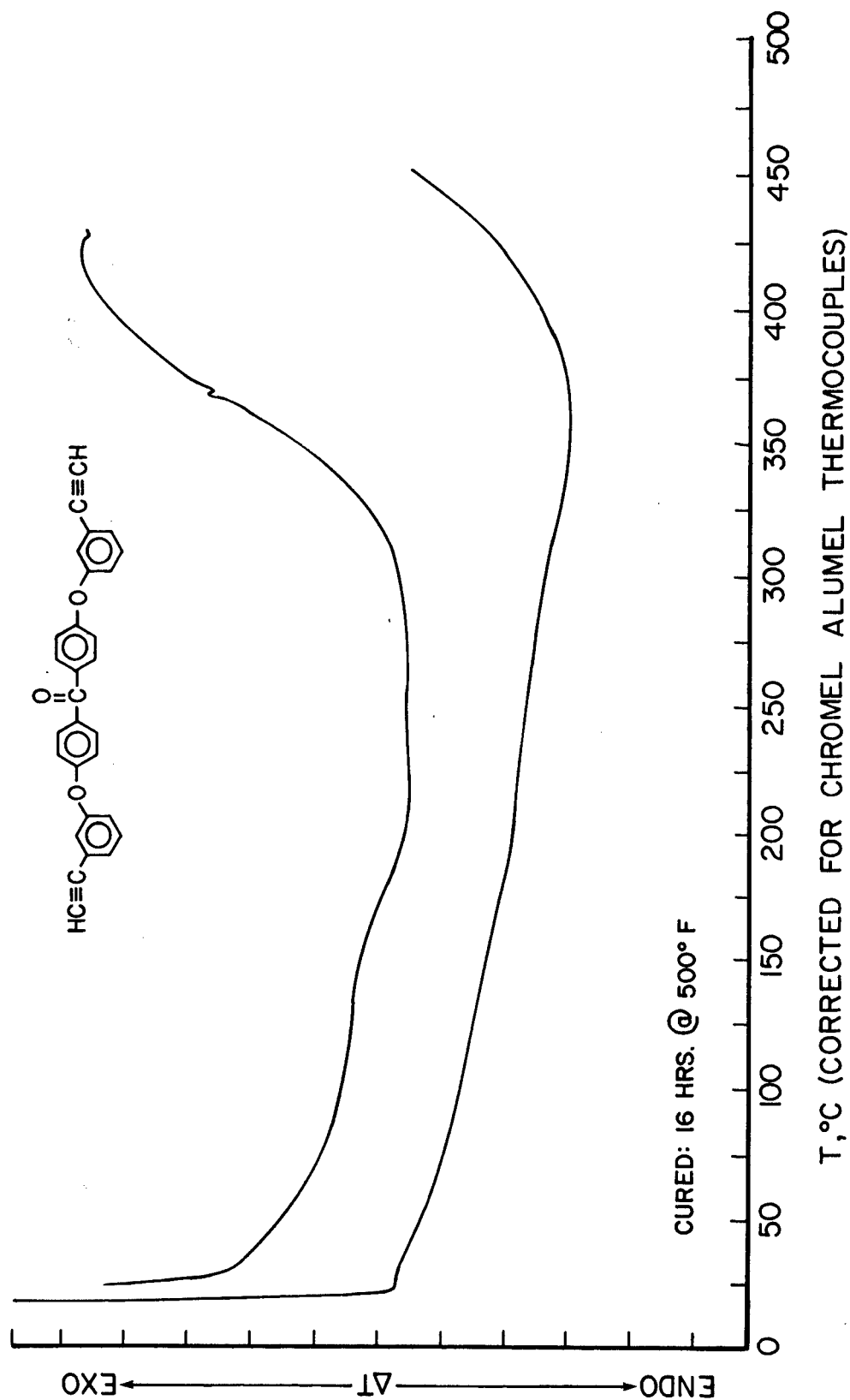


Figure 1. DSC Scan of the Benzophenone System Cured at 500°F for 16 Hours

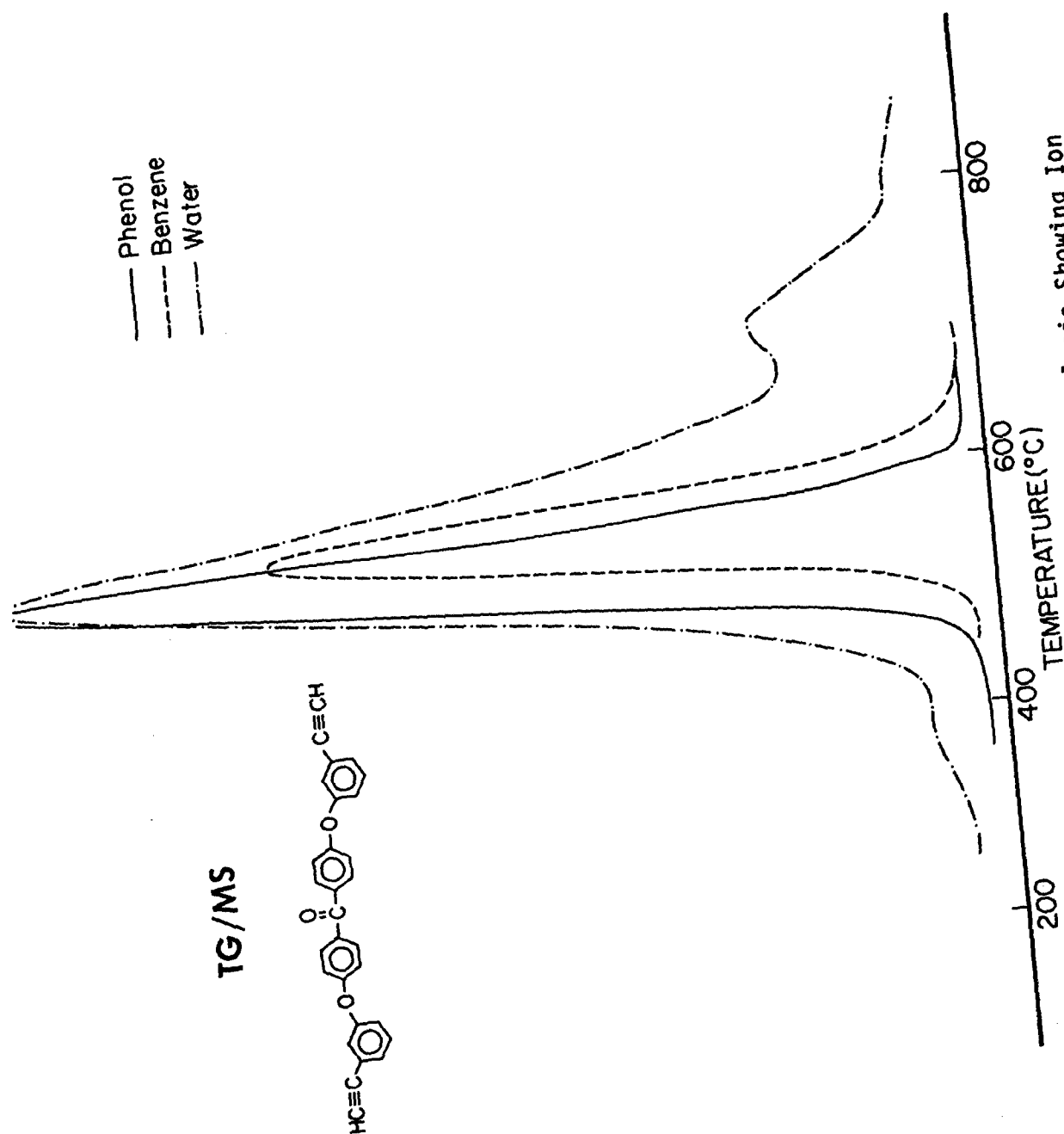


Figure 2. Thermogravimetric-Mass Spectral Analysis Showing Ion Intensity as a Function of Temperature

THERMOGRAVIMETRIC ANALYSIS\*  
IN AIR at 5°C/min

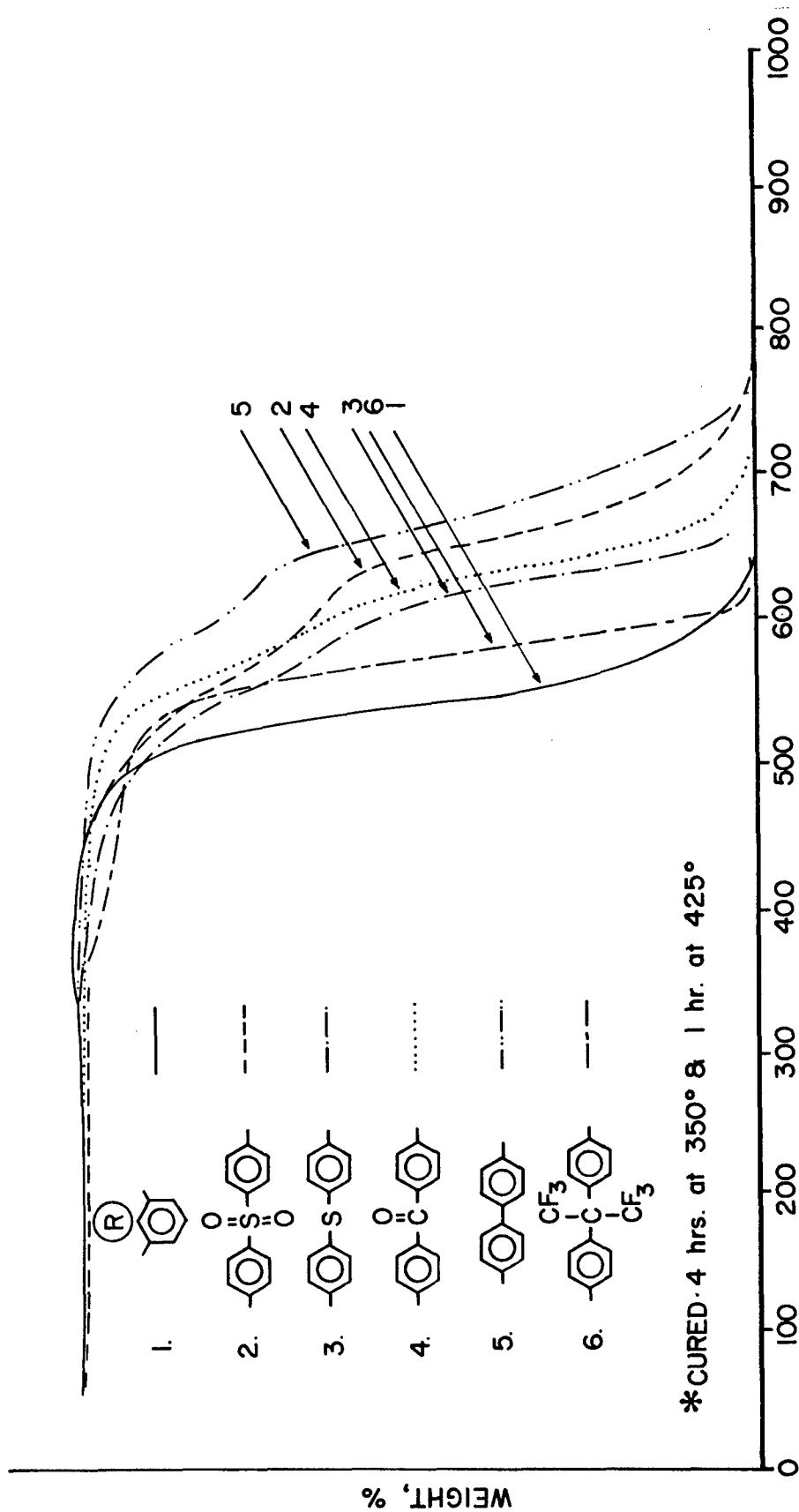
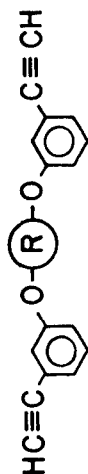


Figure 3. Thermogravimetric Analysis of Cured AT-Phenylene (R)

# THERMOGRAVIMETRIC ANALYSIS\* IN HELIUM at 5°C/min.

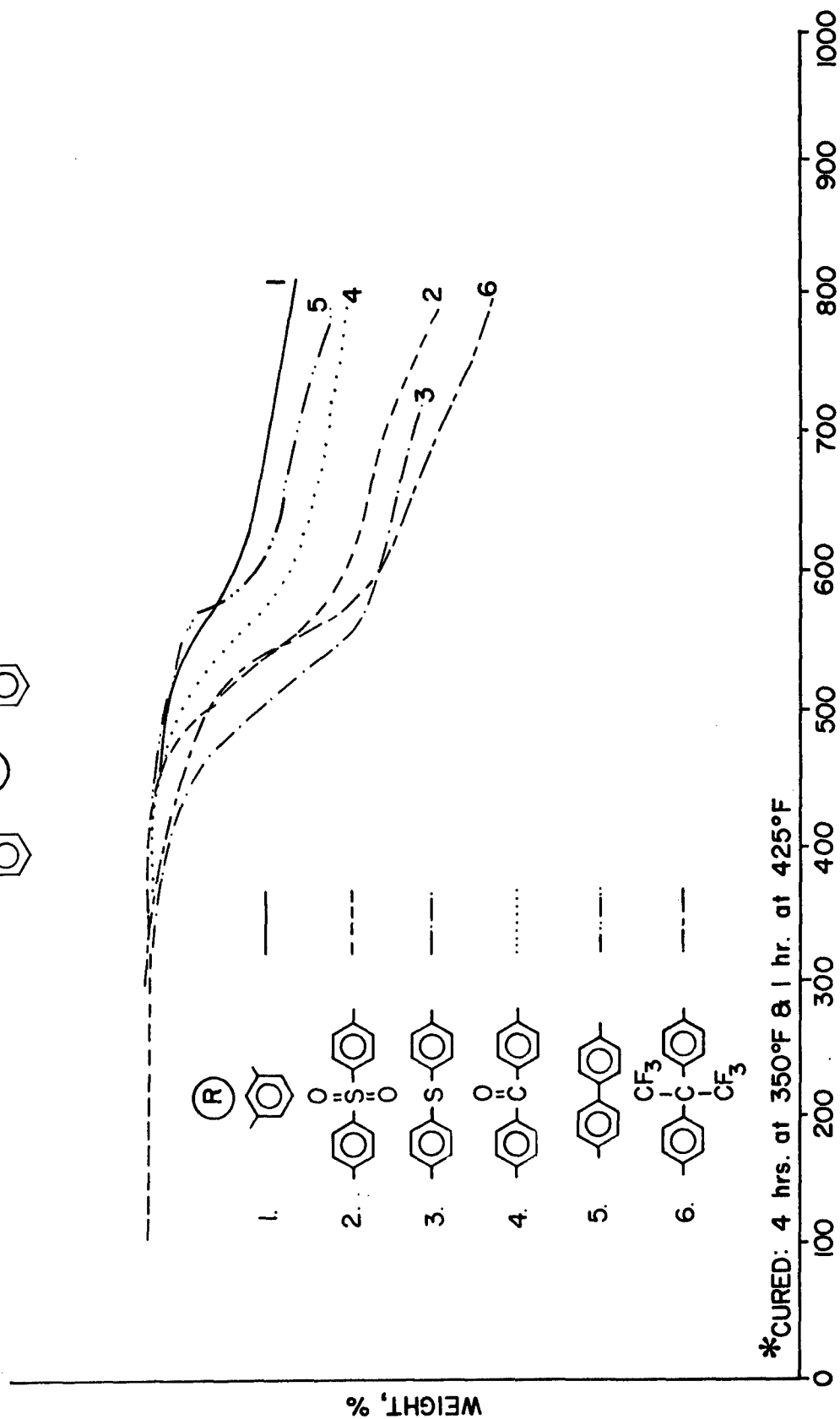
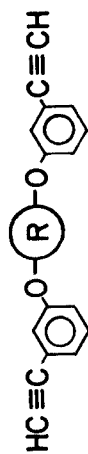
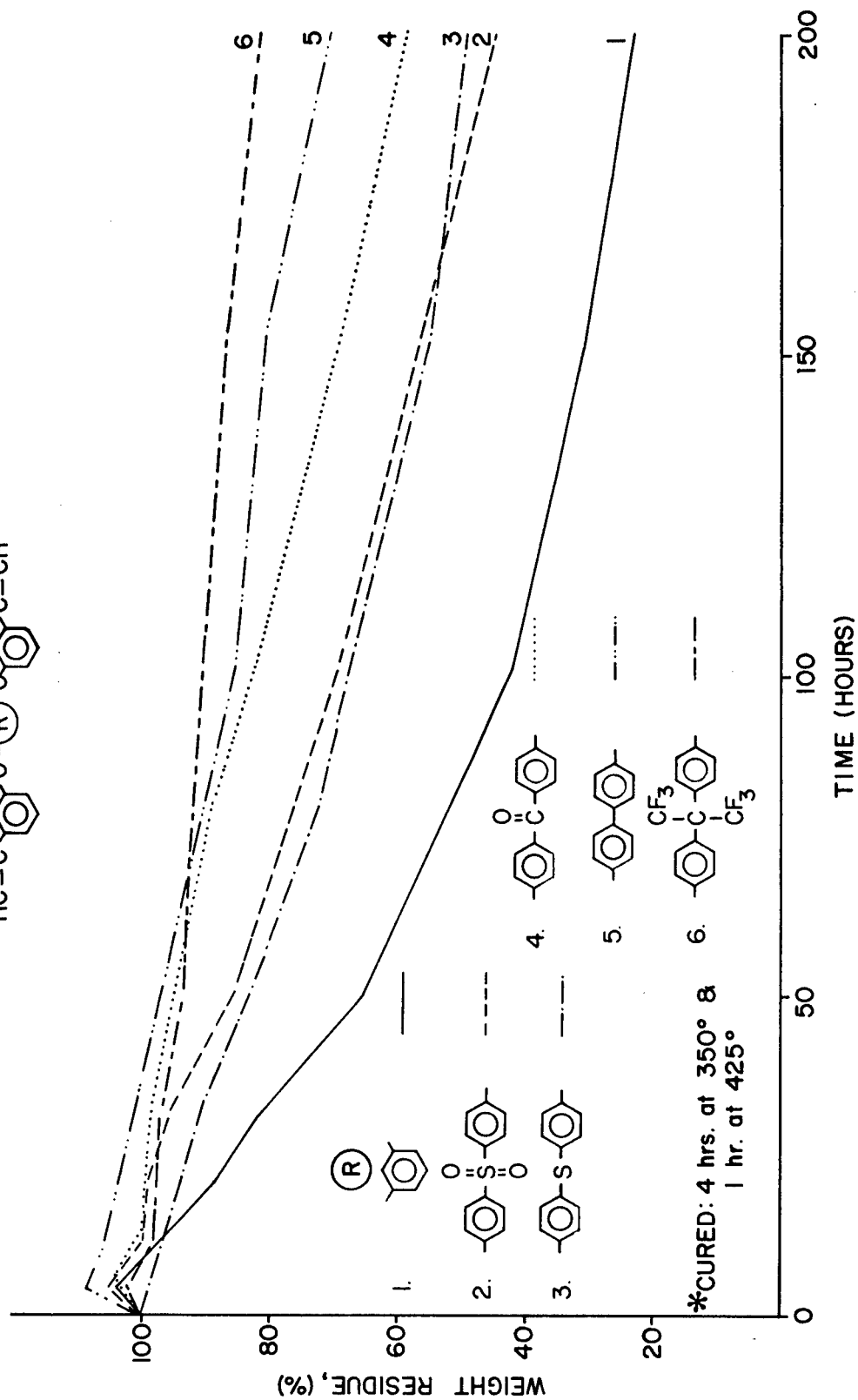
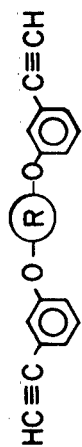


Figure 4. Thermogravimetric Analysis of Cured AT-Phenylene (R) Systems in Helium at 5°C/min.

## ISOTHERMAL AGING\*

600°F in AIR



\*CURED: 4 hrs. at 350° &  
1 hr. at 425°

Figure 5. Isothermal Aging in Air at 600°F of Cured AT-Phenylene (R) Systems (Maximum Cure 425°F)

## ISOTHERMAL AGING\* 600°F IN AIR

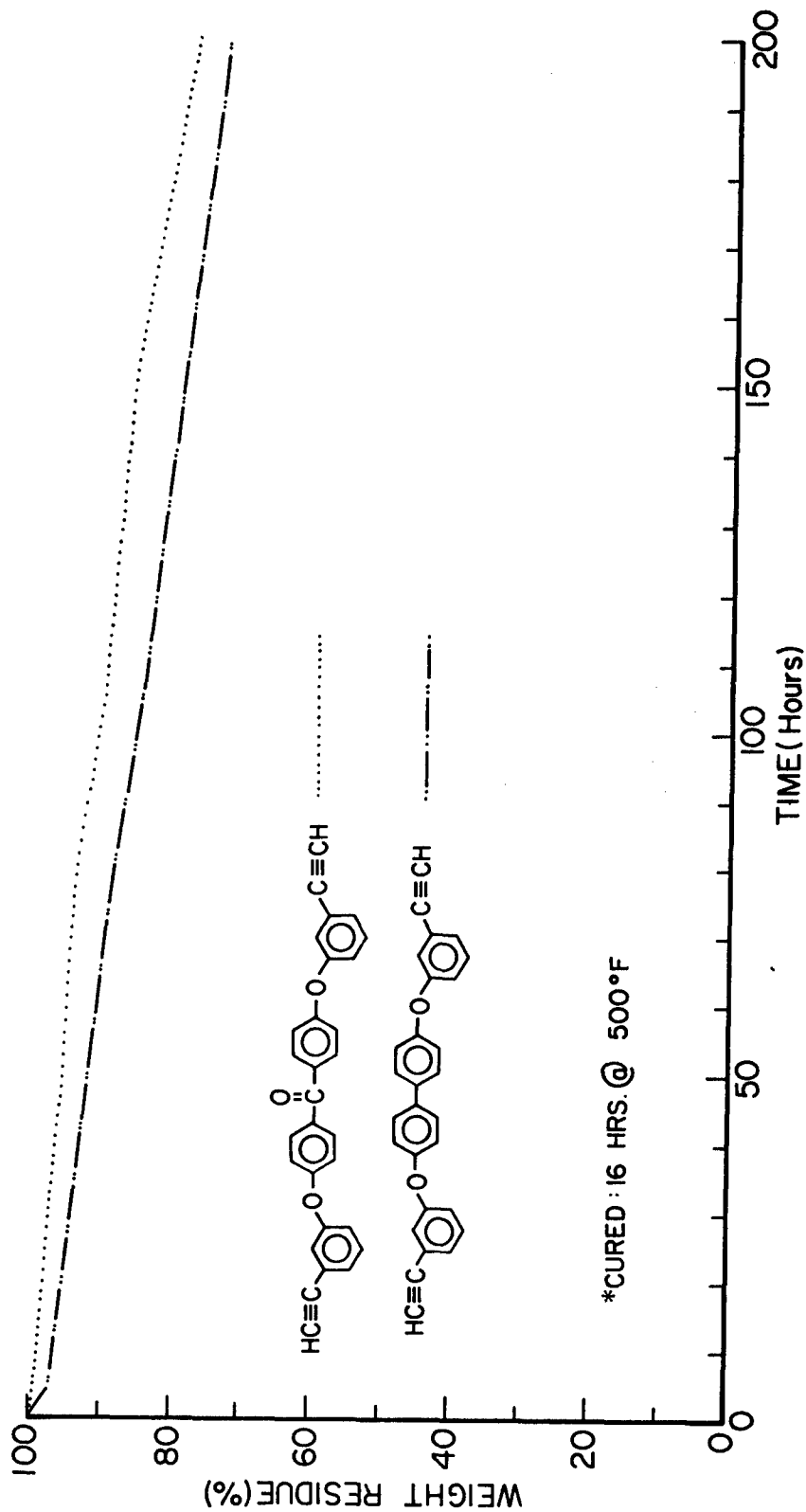
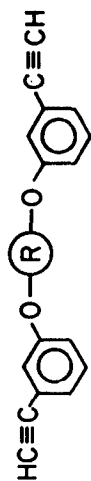


Figure 6. Isothermal Aging in Air at 600°F of Cured AT-Phenylene (R) Systems (Maximum Cure 500°F)



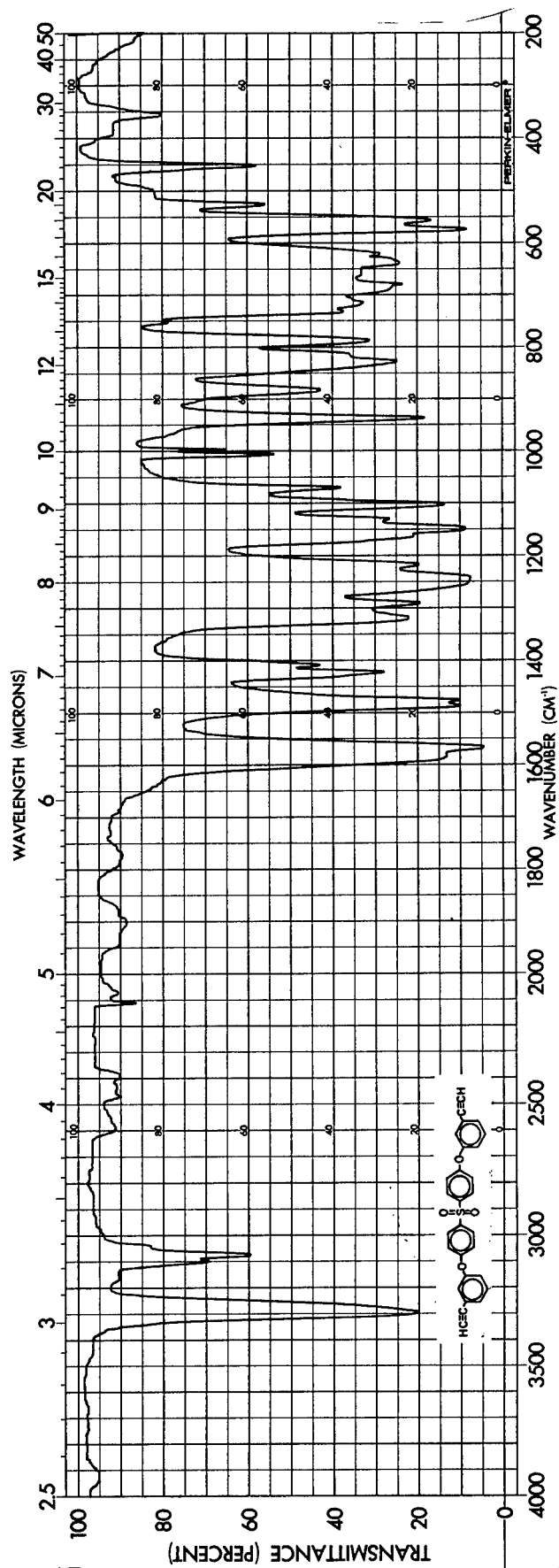


Figure 7. Infrared Spectrum of 4,4'-Bis(3-ethynylphenoxy)-diphenylsulfone

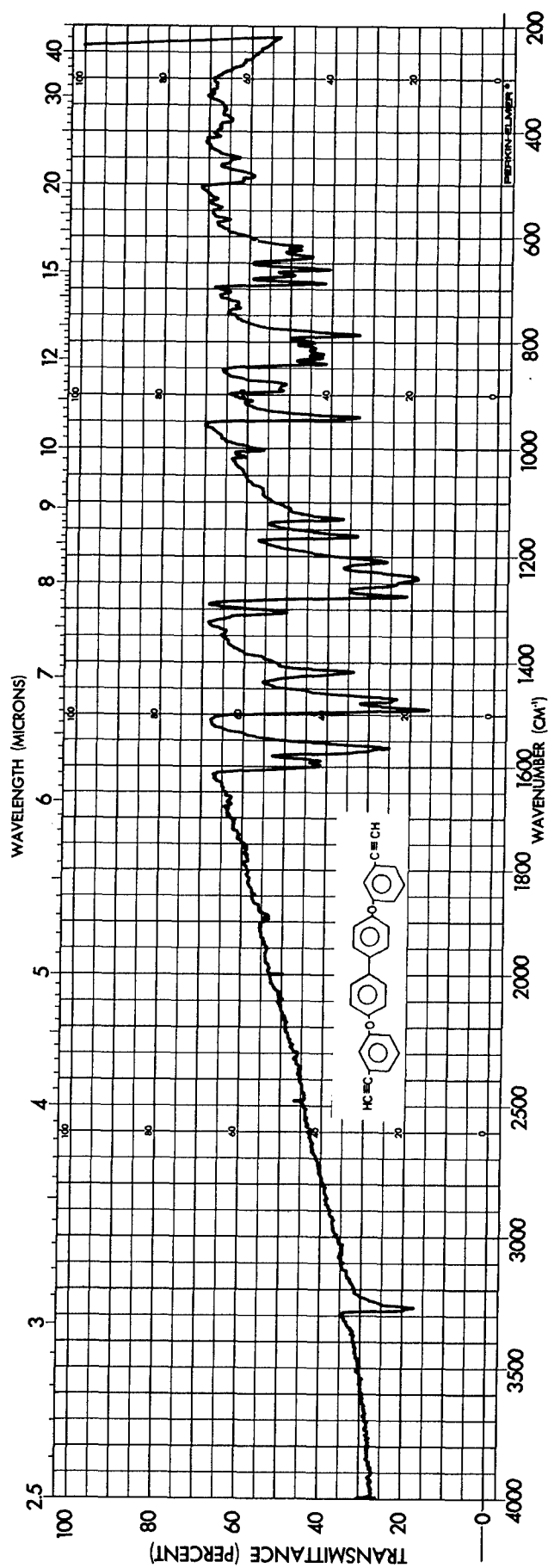


Figure 8. Infrared Spectrum of 4,4'-Bis(3-ethynylphenoxy)-biphenyl

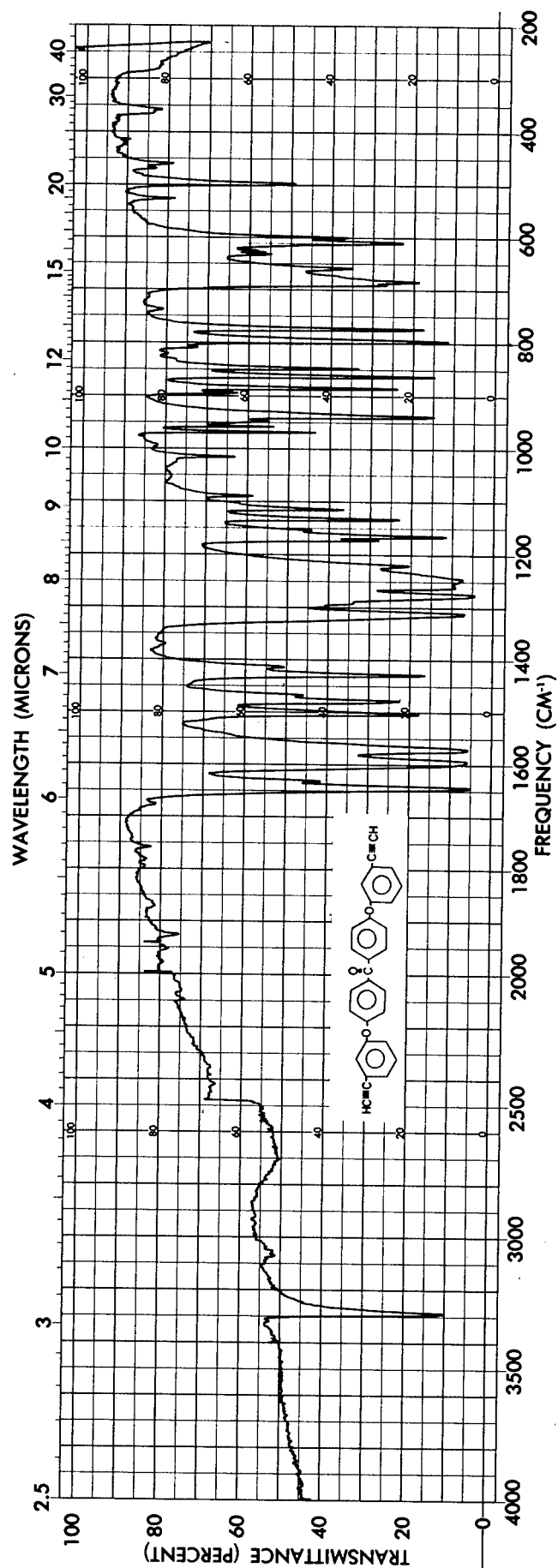


Figure 9. Infrared Spectrum of 4,4'-Bis(3-ethynylphenoxy)-benzophenone

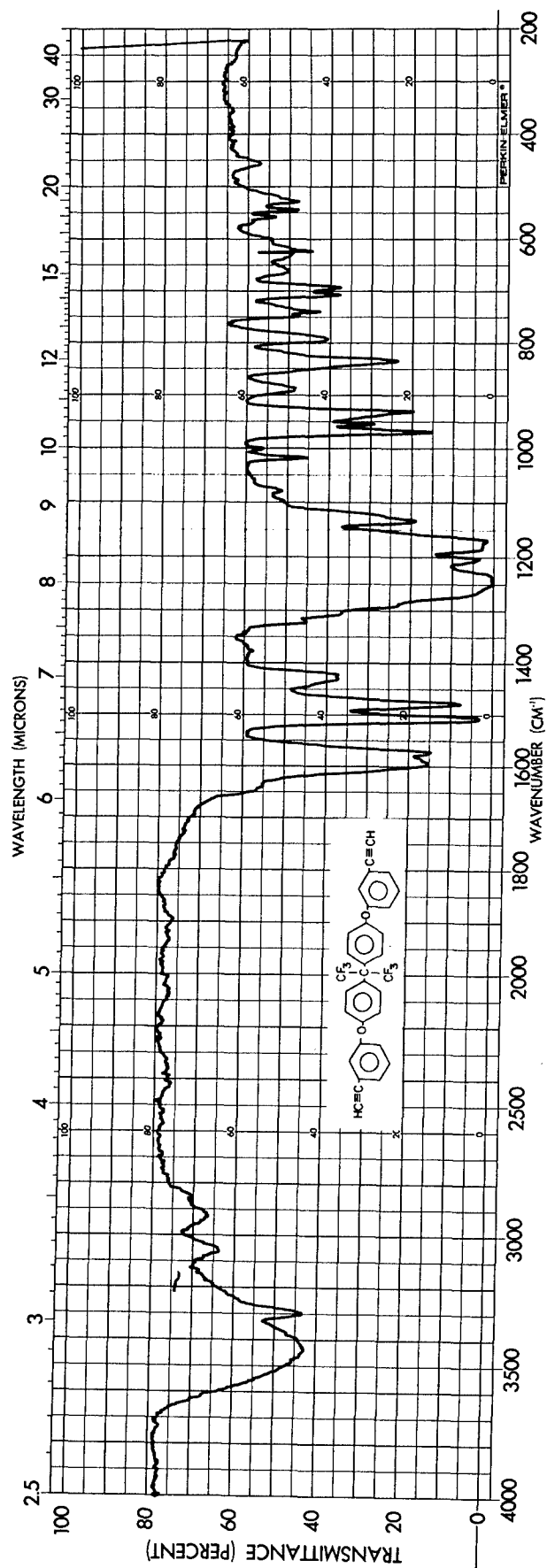


Figure 10. Infrared Spectrum of 4,4'-Bis(3-ethynylphenoxy)-diphenylhexafluoropropane

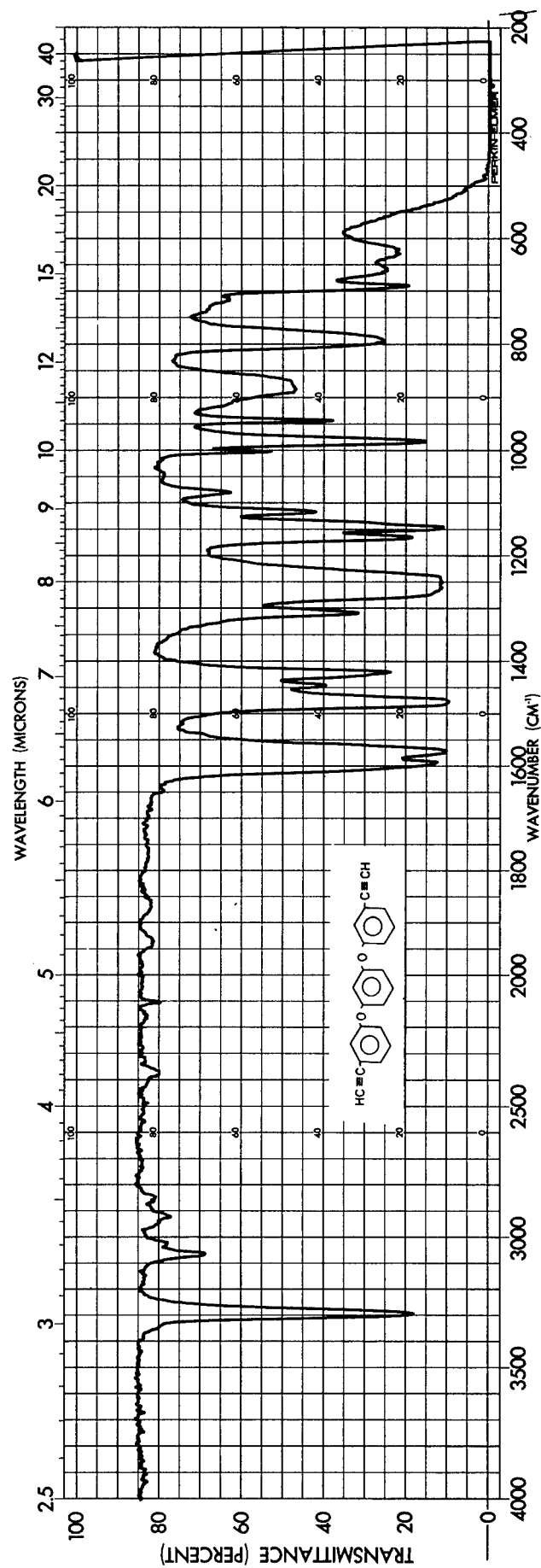


Figure 11. Infrared Spectrum of 1,3-Bis(3-ethynylphenoxy)-benzene

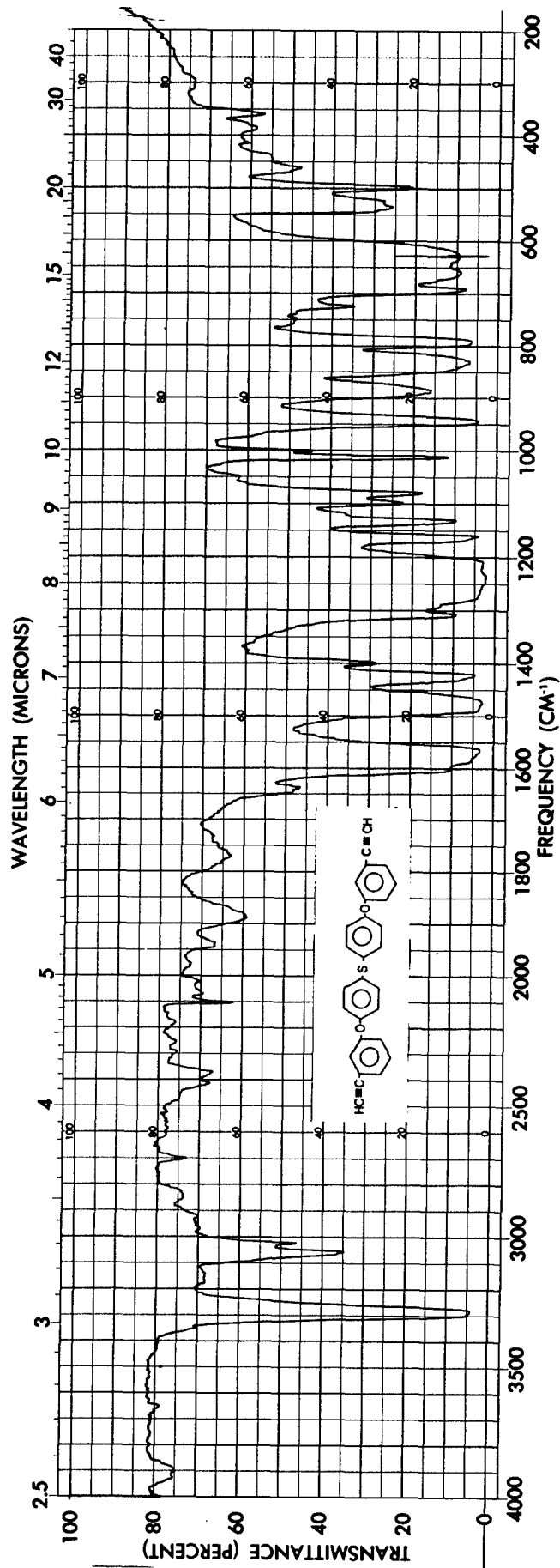


Figure 12. Infrared Spectrum of 4,4'-Bis(3-ethynylphenoxy)-diphenylsulfide